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Synthesis and Spectral Studies of the Bivalent Transition Metal Complexes of 3-Hydroxypicolinamide

R.K. LONIBALA*, T.H. PROMILA DEVI, SHARMELI YUMNAM and R.K. BABITA DEVI†
Department of Chemistry, Manipur University, Canchipur-795 003, India
E-mail: lonirk@yahoo.co.uk

Some bivalent transition metal complexes of 3-hydroxypicolinamide (LH) of the empirical formulae, $[M(LH)_2Cl(H_2O)]Cl$ [M = Mn, Co, Ni, Cd], $[Cu(LH)_2Cl(OH)]$, $[Hg(LH)_2Cl_2]$ and $[M(L)_2(H_2O)n]$ [M = Mn, Co, Ni, Cu, Cd, Hg] have been synthesized. ^{1}H NMR studies suggested the presence of one dissociable proton in the ligand. IR and NMR data show that LH acts as a neutral N,O chelating ligand in the protonated form while it behaves as a uninegative O, O chelating species in the monodeprotonated form. Electronic spectral studies suggest distorted octahedral geometry for Mn(II), Co(II), Ni(II) and Cu(II) complexes. Isotropic nature of Mn(II) complexes and anisotropic nature of Cu(II) complexes at LNT have been inferred from the ESR studies. Appreciable covalent nature of bonding in the complexes is suggested by the bonding parameters obtained from electronic and ESR spectra. ^{113}Cd chemical shift also shows that Cd(II) ion is covalently bonded in $[Cd(LH)_2Cl(H_2O)]Cl$. XRD powder patterns of the Cu(II) complexes are indexed for a tetragonal crystal system for $[Cu(LH)_2Cl(OH)]$ and orthorhombic for $[Cu(L)_2(H_2O)_2]$. Tentative structures of these complexes have been suggested based on their elemental, thermal, molar conductance, magnetic moment, and spectral data.

Key Words: Spectral studies, 3-Hydroxypicolinamide, Bivalent, Transition metal complexes, Protonated, Monoprotonated.

INTRODUCTION

3-Hydroxypicolinyl group is attached to Virginiamycin S (VS) through an amide bond. Virginiamycin S is an the antibiotic which blocks protein synthesis at bacterial ribosomes[1], inhibits respiration in rat liver and yeast mitochondria[2] and is reported[3] to behave as general cation carrier. The biological activities of virginiamycin S were exclusively attributed to the physicochemical properties of the 3-hydroxypicolinyl residue. The loss of antimicrobial power of virginiamycin S[4] when the picolinyl moiety was replaced by a serene derivative, indicates that the 3-hydroxypicolinyl residue is essential for its antibiotic activity. Thus, for the study of chelating ability and fluorescence of virginiamycin S, 3-hydroxypicolinamide is used[5-7] as a model compound. The results obtained by Giambattista *et al.*[5] indicated that alkaline earth cations

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†Department of Chemistry, Imphal College, Manipur-795 001, India.

probably coordinate to the twice-deprotonated form of 3-hydroxypicolinamide and a complexation of these cations by the phenolate oxygen is likely to take place with the participation of the amide carboxyl group. However, in the Zn(II) complex of 3-hydroxypicolinamide reported by Sakai *et al.*[8], the amide coordinates through the ring N and the carbonyl oxygen in the protonated form as a neutral species, not through the phenolate oxygen atom. Therefore, in order to understand more about the complexation behaviour of 3-hydroxypicolinamide (LH, Fig. 1) towards the metal ions, we have synthesized some transition metal complexes of this compound and carried out a systematic study on the complexes.

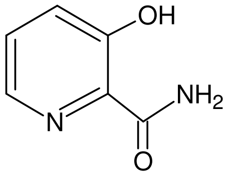


Fig. 1. Structure of 3-hydroxypicolinamide (LH)

EXPERIMENTAL

3-Hydroxypicolinamide (LH) was obtained from Sigma-Aldrich and was used as such. All the chemicals used were of BDH, AR grade. The complexes were analyzed for the element contents employing literature procedures[9]. C, H and N were microanalyzed. Thermal studies are carried out with a Shimadzu thermal analyzer DT-30. Molar conductance was measured in DMSO at room temperature on a WTW conductivity meter. Magnetic susceptibility measurements were carried out on a magnetic susceptibility balance, sherwood scientific Cambridge, U.K. while the electronic spectra were recorded on Cary-14 spectrophotometer. A Perkin Elmer IR spectrophotometer model 783 was used for taking the IR spectra. The ESR spectra were obtained on a Varian E-12 X-band spectrometers and NMR spectra on a Jeol FX-90Q multinuclear NMR spectrometer using appropriate probe. The X-ray powder diffraction data of the Cu(II) complexes were taken on a Phillips X-ray diffractometer, PW 1710 using CuK_α radiation. The FAB mass spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon as the FAB gas.

Preparation of complexes: $[M(LH)_2Cl(H_2O)]Cl$ [M = Mn, Co, Ni, Cd] (**1a, 2a, 3a, 5a**), $[Cu(LH)_2Cl(OH)]$ (**4a**) and $[Hg(LH)_2Cl_2]$ (**6a**) were prepared from the ethanolic solutions of the appropriate metal chloride (1 mmol in 10 mL) and LH (2 mmol in 20 mL). $[Mn(LH)_2Cl(H_2O)]Cl$ (**1a**) was formed upon addition of acetonitrile (30 mL) to the concentrated solution of the reaction mixture of manganese chloride (990 mg; 1 mmol in 10 mL ethanol) and LH (1300 mg; 2 mmol in 20 mL ethanol), with vigorous stirring. The precipitated complex was washed with acetonitrile and dried *in vacuo*. The complexes $[Co(LH)_2Cl(H_2O)]Cl$ (**2a**) and $[Ni(LH)_2Cl(H_2O)]Cl$ (**3a**) were precipitated on keeping the reaction mixture overnight after refluxing for **4h**, while [Cu(LH)$_2$Cl(OH)] (**4a**), [Cd(LH)$_2$Cl(H$_2$O)]Cl (**5a**) and [Hg(LH)$_2$Cl$_2$] (**6a**) were obtained within few seconds of mixing the ethanolic solutions. The precipitated complexes were filtered off, washed several times with a mixture of acetonitrile and ethanol (50:50 v/v) and dried in air. Yield 60-70 %.

[M(L)$_2$(H$_2$O)$_2$] [M = Mn, Co, Ni, Cu, Cd, Hg] (**1b, 2b, 3b, 4b, 5b, 6b**) were prepared by mixing aqueous solutions of the appropriate metal chloride (1 mmol in 10 mL) and LH (2 mmol in 20 mL) and adjusting the pH of the resulting solution at *ca.* 7 by the controlled addition of 1 N KOH solution. The precipitated complexes were digested on a water bath for 0.5 h, cooled, filtered, washed successively with water, ethanol and ether and dried at room temperature. Yield 60-70 %.

RESULTS AND DISCUSSION

The analytical data (Table-1) shows that 3-hydroxypicolinamide reacts with metal ions to form both addition and neutral complexes in 1:2 metal-ligand ratio.

TABLE-1
PHYSICAL CHARACTERISTICS, ANALYTICAL AND MOLAR CONDUCTANCE DATA (Ω^{-1} cm^2 mol^{-1}) OF THE COMPLEXES OF 3-HYDROXYPICOLINAMIDE (LH)

Complex	Colour	Found (calcd.) %					Molar conductance
		C	H	N	M	Cl	
[Mn(LH)$_2$Cl(H$_2$O)]Cl (**1a**)	Light yellow	34.51	2.90	13.03	13.41	17.35	88.26
		(34.29)	(3.33)	(13.34)	(13.08)	(16.91)	
[Co(LH)$_2$Cl(H$_2$O)]Cl (**2a**)	Light pink	32.69	3.39	12.39	13.05	15.60	38.29
		32.58	3.62	(12.67)	(13.33)	(16.06)	
[Ni(LH)$_2$Cl(H$_2$O)]Cl (**3a**)	Grey	33.62	3.51	13.46	13.81	16.99	74.68
		33.99	3.30	(13.22)	(13.86)	(16.76)	
[Cu(LH)$_2$Cl(OH)] (**4a**)	Bluish green	33.47	3.55	13.21	14.74	8.40	5.77
		33.64	3.50	(13.08)	(14.84)	(8.29)	
[Cd(LH)$_2$Cl(H$_2$O)]Cl (**5a**)	Grey	29.91	2.34	12.00	23.59	15.05	84.87
		30.16	2.93	(11.73)	(23.54)	(14.87)	
[Hg(LH)$_2$Cl$_2$] (**6a**)	White	25.78	2.10	9.78	36.78	12.87	7.92
		26.30	2.19	(9.86)	(36.63)	(12.97)	
[Mn(L)$_2$(H$_2$O)$_2$] (**1b**)	Light yellow	38.30	4.17	15.12	14.90	–	–
		39.46	3.84	(15.35)	(14.93)		
[Co(L)$_2$(H$_2$O)$_2$] (**2b**)	Light pink	38.04	3.60	14.97	15.88	–	–
		39.03	3.79	(15.18)	(15.97)		
[Ni(L)$_2$(H$_2$O)$_2$] (**3b**)	Light green	39.49	3.68	15.19	15.83	–	8.49
		39.06	3.80	(15.19)	(15.92)		
[Cu(L)$_2$(H$_2$O)$_2$] (**4b**)	Green	41.67	2.67	16.54	18.81	–	–
		42.66	2.96	(16.59)	(18.83)		
[Cd(L)$_2$(H$_2$O)$_2$] (**5b**)	Cream	33.89	3.10	13.78	26.45	–	–
		34.09	3.14	(13.76)	(26.61)		
[Hg(L)$_2$(H$_2$O)$_2$] (**6b**)	Light yellow	28.20	2.52	10.62	39.30	–	–
		28.20	2.74	(10.58)	(39.29)		

d: Decomposition temperature.

Formation of the former type of complexes is favoured in weakly acidic condition while the deprotonated/neutral complexes are isolated from mildly basic media. All the complexes are stable and didn't melt until 250 ºC, except (**6a**) which decomposes at 183 ºC. The complexes (**4a, 6a, 1b, 2b, 3b, 4b, 5b** and **6b**) are non-electrolytes while the complexes (**1a, 2a, 3a, 5a**) behave as 1:1 electrolytes in 0.001 M DMSO solutions[10]. Infrared spectra and thermogravimetric curves of all the complexes except **6a** indicate the presence of water molecules. Thermogravimetric curves in the range (100-700 ºC) show that mass loss corresponding to one molecule of water for complexes (**1a, 2a, 3a, 4a, 5a**) and two molecules of water for (**1b, 2b, 3b, 4b, 5b** and **6b**) occurs within 500-600 ºC. Loss of H_2O molecules at higher temperature and the presence of a band in 725-715 cm^{-1} region, characteristic of coordinated water[11] in the infrared spectra of these complexes indicate the presence of coordinated water. Such characteristic band is absent in the IR spectrum of **6a**.

Magnetic moment and electronic spectral data: The μ_{eff} and the electronic spectral data of the complexes are given in Table-2. Mn(II) complexes (**1a** and **1b**) show μ_{eff} values slightly lower than the value expected for a spin-free configuration and do not suggest any specific stereochemistry. However, their electronic spectra exhibit only one weak band each suggesting an octahedral environment around Mn^{2+} ion[12]. The μ_{eff} values and absorption spectral profile of Ni(II) complexes, **3a** and **3b**, are compatible with octahedral geometry[13-15]. The magnetic moment values of Cu(II) complexes are normal for one unpaired electron. However, the absorption bands observed in the spectra of the complexes **4a** and **4b** are broad and considerably blue-shifted compared with the first band maxima of the corresponding Ni(II) complexes, **3a** and **3b** due to Jahn-Teller distortion of the ^2E_g state, suggesting a tetragonally distorted Cu(II) complex[12,16]. The charge transfer band at 25641 cm^{-1} for **4b** may be attributed to the phenolato to copper CT transition[17]. The magnetic moment values of the Co(II) complexes, **2a** and **2b** indicate a spin quartet ground state, though the values are lower than the ranges reported for both tetrahedral (4.4-4.8) and octahedral (4.7-5.3) Co(II) complexes. However, the three medium intense bands observed in both the electronic spectra of **2a** and **2b** suggest an octahedral geometry[12].

TABLE-2
MAGNETIC MOMENT (μ_{eff}) AND ELECTRONIC SPECTRAL DATA ALONG WITH THE ASSIGNED TRANSITIONS OF THE COMPLEXES

Complex	μ_{eff} (BM)	Absorption bands (cm^{-1})	Transitions
1a	5.61	15625	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
2a	4.12	9090, 14286, 21053	$^4T_{1g} \rightarrow {}^4T_{2g}, {}^4A_{2g}$ (F), $^4T_{1g}$ (P)
3a	3.15	8696, 15267, 21505	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^3T_{1g}(F), {}^3T_{1g}(P)$
4a	1.92	13106	$^2B_{1g} \rightarrow {}^2A_{1g}$
1b	5.79	17391	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
2b	4.17	9756, 13333, 20833	$^4T_{1g} \rightarrow {}^4T_{2g}, {}^4A_{2g}$ (F), $^4T_{1g}$ (P)
3b	2.97	10363, 14286, 23256	$^3A_{2g} \rightarrow {}^3T_{2g}, {}^3T_{1g}(F), {}^3T_{1g}(P)$
4b	1.79	15152	$^2B_{1g} \rightarrow {}^2A_{1g}$

Infrared spectra: The IR spectrum of the ligand exhibits bands at 1690, 1515, 1300 and 1200 cm^{-1} due to amide I, amide II, amide III and ν_{sym}(CO), respectively. A negative shift in amide I (30-60 cm^{-1}) and amide II (10-60 cm^{-1}) and a positive shift (5-45 cm^{-1}) in amide III observed in the spectra of all the complexes suggest the coordination of the carbonyl oxygen to the metal ions[17]. The bands at 1015 and 550 cm^{-1} due to wagging and rocking NH_2 remain unaltered in the spectra of the complexes thereby showing the non-involvement of NH_2 in bonding. In the spectra of the deprotonated complexes (**1b, 2b, 3b, 4b, 5b, 6b**), a positive shift in $\nu_{sym}(CO)_{phenolic}$ (5-10 cm^{-1}) and the appearance of a new band likely due to ν_{asym}(COM) in the 1565-1520 cm^{-1} region indicate bonding through the phenolate oxygen[18]. The pyridine ring vibrations show bathochromic shift at 1050-985, 690-665 and 450-410 cm^{-1} in the spectra of all the adducts (**1a, 2a, 3a, 4a, 5a, 6a**) showing coordination of pyridine ring nitrogen[19] whereas these bands do not show any shift in the deprotonated complexes. For the complex **4a**, elemental analysis data showing the presence of only one chlorine atom and its nonelectrolytic behaviour suggest that the chlorine atom is inside the coordination sphere. The charge balance of the molecular formula for **4a** requires that deprotonation of a water molecule occurs and participates in the complex formation as a hydroxide ion as one of the axial ligands. Similar type of bonding is reported for Zn(II) complex[8]. Formation of a Cu-OH bond[20] is also indicated by the appearance of an intense band characteristic of MOH bonding at 1155 cm^{-1} in the spectrum of **4a**. The non-ligand bands in the regions 305-375, 325-355 and 265-295 cm^{-1} are tentatively assigned to ν(M-O), ν(M-N) and ν(M-Cl), respectively. Singlet nature of M-Cl band in the spectrum of **6a** shows the two chlorine atoms to be in the *trans*-position.

Electron spin resonance spectra: The RT and LNT ESR spectra of Mn(II) complexes (**1a** and **1b**) are isotropic and consist of sextets arising due to the hyperfine interaction between the unpaired electrons and the ^{55}Mn nucleus (I = 5/2). However, the line-shape of the spectra is characteristic of an asymmetrical ligand arrangement around the Mn^{2+}. The line-broadening observed in the spectrum of complex (**1a**) is noticeably larger than that of (**1b**), suggesting a strong distortion in the stereochemistry of the former complex from the cubic symmetry[21]. The g_{iso} and A_{iso} values are given in Table-3. The ESR spectra of complexes (**4a**) and (**4b**) are isotropic at room temperature but anisotropic in nature at 77 K. No half field signal was observed in the spectra suggesting monomeric nature of the complex (Fig. 2). The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) (Table-3) indicates tetragonal elongation along the Z-axis and presence of the unpaired electron in the $d_{x^2-y^2}$ orbital[22]. The observed $g_{\parallel}$ values for **4a** and **4b** are less than 2.3 in agreement with the covalent character of the metal ligand bond. Appreciable covalent bonding is also supported by the s-bonding parameter, α^2, which fall at 0.75 and 0.45, respectively. The geometric parameter, $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid has been calculated. If G > 4, the exchange interaction is negligible and if G < 4, a considerable exchange interaction is indicated[23]. In the complex (**4a**), G

= 4.75, showing negligible exchange interaction. A relatively high $A_{\|}$ value (>150 × 10^{-4}) also suggests small axial interaction. G for (**4b**) = 2.03 indicates that there is some exchange interaction in this solid complex.

TABLE-3
ESR SPECTRAL PARAMETERS OF THE Mn(II) AND Cu(II) COMPLEXES OF 3-HYDROXYPICOLINAMIDE

Complex	$g_{\|}$	$g_{\perp}$	g_{iso}	$A_{\|}$ (G)	$A_{\perp}$ (G)	A_{iso} (G)	α^2	G
1a	–	–	1.990	–	–	94.0	–	–
1b	–	–	1.997	–	–	84.0	–	–
4a	2.227	2.057	2.146	161.7	31.7	56.7	0.75	4.75
4b	2.150	2.074	2.160	–	26.7	–	0.48	2.03

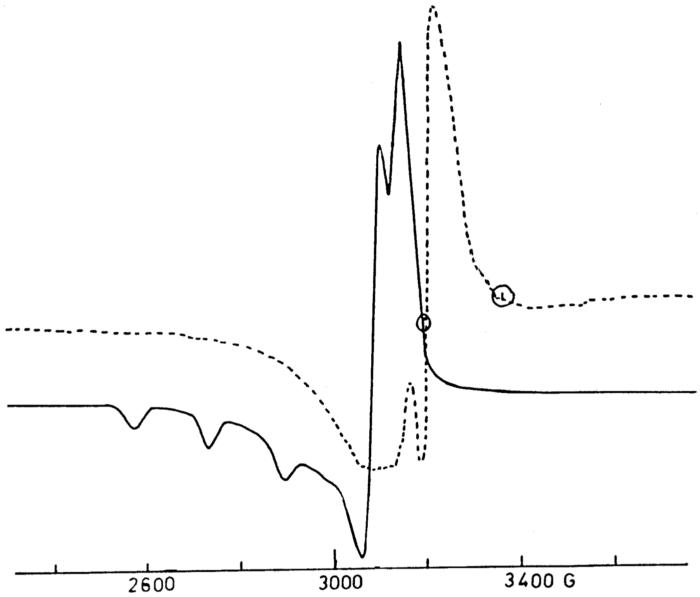


Fig. 2. ESR spectra of $[Cu(LH)_2Cl(OH)]$ (**4a**) at RT (----) and LNT (—)

X-Ray powder diffraction studies: The X-ray powder diffraction of these complexes yield a number of diffraction lines indicating crystalline nature of the complex. The observed interplanar spacings have been satisfactorily indexed[24] for tetragonal symmetry for (**4a**) and orthorhombic symmetry for (**4b**) by Hesse-Lipson's method. The lattice parameters calculated for the above symmetries are as follow:

4a: a = b = 11.84 Å; c = 11.728 Å

and **4b**: a = 6.3677 Å; b = 6.0311 Å; c = 5.7813 Å

Nuclear magnetic resonance spectra: The ^{1}H NMR assignments have been made on the calculated values and the spectral data of LH and complexes **5a** and **6a** are given in Table-4. Deuterium exchange of LH was used to determine the signals due to -OH. The singlet due to hydroxyl proton remains almost unchanged in the spectra of these complexes suggesting non-involvement of the hydroxyl group in complexation. However, it vanishes in those of the deprotonated complexes (**5b**, **6b**) indicating the deprotonation of LH and complexation of the amide as (L^-) to the metal(II) ion through phenolate oxygen. The NH_2-protons which resonate at δ 3.33 in the metal-free ligand spectrum show no significant shift showing its non-involvement in complexation. The line broadening in the signals of -OH and NH_2-protons in the spectrum of **5a** and their shift for **6a** may be due to the intramolecular hydrogen bond formation between the amino hydrogen and hydroxyl oxygen $N\text{-}H\cdots O$[25]. This intramolecular hydrogen bonding might restrict the deviation of the amide plane from the pyridine plane when chelating a metal ion and stabilize the complexes. It has also been shown that both intra- and intermolecular hydrogen bonding are observed in Cd(II)[25] and Co(II)[26] complexes of 3-hydroxypicolinic acid and Zn(II) complex of 3-hydroxypicolinamide[8]. Participation of the ring nitrogen in bonding[27] in the adducts has been suggested from the shifts and change in the nature of the signals due to ring protons, probably due to the shielding of ring current upon coordination while these signals remain almost at the same position in the spectra of the deprotonated complex (**5b, 6b**) showing its non-participation in bonding.

TABLE-4
^{1}H AND ^{13}C NMR DATA* OF 3-HYDROXYPICOLINAMIDE AND ITS Cd(II) AND Hg(II) COMPLEXES

	LH	**5a**	**6a**	**5b**
$\text{-O}\underline{\text{H}}$	12.86^{s}	12.79^{b}	12.76^{s}	–
$\text{-N}\underline{\text{H}}_2$	3.33	3.38^{b}	3.80	3.54
Ring protons	8.57^{s}, 8.17^{s}, 7.48^{m}	8.55^{s}, 7.79^{s}, 6.99^{m}	8.13^{b}, 7.71^{s}, 6.93^{m}	8.55^{b}, 8.19^{s}, 7.97^{m}
$>\underline{\text{C}}\text{O}$	172.32	171.05	171.74	–
C(2)	131.43	131.11	131.33	–
C(3)	158.05	157.74	157.76	–
C(4)	126.04	126.04	125.80	–
C(5)	129.53	129.21	129.32	–
C(6)	139.99	139.67	139.83	–

*Measured in ppm with respect to DMSO-d_6 (39.50 ppm). b: broad; s: singlet; m: multiplet.

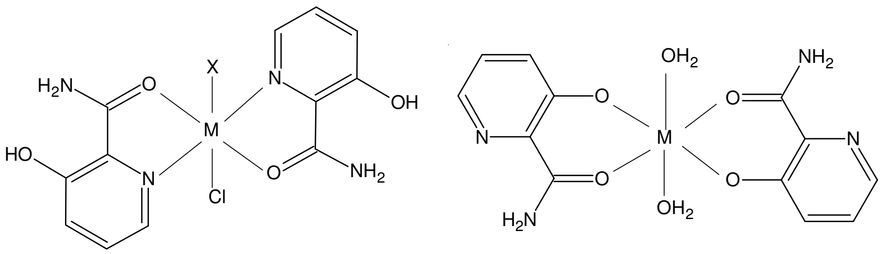
The ^{13}C NMR spectra of LH and its metal complexes (**5a** and **6a**) were recorded in DMSO-d_6 while the chemical shifts of all the assigned groups are also collected in Table-4. The signal corresponding to the amide carboxyl carbon is shifted upfield by 1.27 and 0.58 ppm for **5a** and **6a**, respectively upon complex formation which may be ascribed as due to the molecular field effect[28]. Coordinated pyridine ring shows upfield shift for C(2) and C(6) and downfield shift for C(3), C(4) and C(5)[29]. Surprisingly it is not true for these addition complexes having coordinated pyridine ring. The C(2) and C(3) carbons was shifted upfield by 0.32 ppm for **5a** and downfield for **6a**. The C(4) and C(6) ring carbon resonances show downfield shift for **6a** and upfield shift for **5a**. The signal due to C(5) ring carbon at 126.04 ppm remain unshifted in the spectra of **5a** and **6a**. The differences in the nature of the shifts in the ^{13}C resonances may be attributed to the different factors governing the shifts[30] or to the fact that the variation in the charge distribution around the pyridine ring which occurs on coordination is dependent both on the metal and any other coordinated ligand(s)[31].

^{113}Cd NMR spectrum of the complex **5a** is carried out at 25 ºC in DMSO-d_6. The chemical shift was referenced to external 1 M $CdSO_4$ in D_2O which resonates at 2.81 ppm which is taken as 0.00 on the scale. A negative value for a chemical shift denotes a resonance to lower shielding while a positive chemical shift denotes resonances to higher shielding. The cadmium halides CdI_2, $CdBr_2$ and $CdCl_2$ range in chemical shift from -55.13 to -108.60 ppm while the chemical shifts of highly covalent organocadmium compounds range from -489.11 to -642.23 ppm with respect to 0.1 M $Cd(ClO_4)_2$. Highly deshielded nature of these organocadmium compounds is due the introduction of covalent bonds which, in turn, gives rise to a large and negative paramagnetic contribution to the shielding constant[32]. The ^{113}Cd chemical shift of **5a** is at -344 ppm which is very close to that of $Cd(C_6H_5)_2$ in *p*-dioxane (-328.80 ppm). The highly deshielded nature of this resonance shows that the metal ion is covalently bonded. Covalent nature of bonding in the complexes of LH is also supported by the nephelauxetic parameter obtained from the electronic spectra of nickel (**3a, 3b**) and cobalt (**2a, 2b**) complexes and *s*-bonding parameter obtained from ESR spectral data of copper complexes (**4a, 4b**).

Mass spectra: In positive ion FAB mass spectra of two complexes $[Cu(LH)_2Cl(OH)]$ (**4a**) m/z = 390 and $[Cu(L)_2(H_2O)_2]$ (**4b**) m/z = 371, the M^+ of LH m/z = 137 appears as a base peak with 100 % intensity. The spectra of LH and its Cu(II) complexes include peaks corresponding to m/z > molecular mass number which are most likely to suggest the rearrangement of the fragments or collision of the molecular ions with neutral atoms or molecules. In the spectrum of **4a**, the intense peak at (M-150) m/z = 242 which occurs with 80 % intensity for the fragment (M-OH-Cl-C_5H_4NO), peak at m/z = 201 with 50 % intensity for the fragment (M-OH-Cl-LH) and peaks at m/z 374 for (M-OH), 356 for (M-Cl) and 339 for (M-OH-Cl) which occur with 20 % intensity are taken as confirmation of the M^+ at m/z = 392. The M^+ peak for **4b** m/z = 371 occurs with 50 % intensity. Thus, the mass spectra of the Cu(II) complexes (**4a, 4b**) confirm the molecular formula proposed based on the elemental and spectroscopic studies.

Conclusion

Elemental analysis data show that 3-hydroxypicolinamide (LH) can form complexes with bivalent metal ions in the 1:2 metal-ligand stoichiometry. IR and NMR spectral data indicates that LH is a potential ligand with different chelating modes depending upon the media in which the complexation was carried out and LH acts as a neutral N,O-chelating ligand in the protonated form, coordinating through pyridinic ring nitrogen and amide carbonyl oxygen or a uninegative O,O-chelating ligand in the monodeprotonated form, bonding through phenolate oxygen and amide carbonyl oxygen. Based on the above discussions, the tentative structures of the metal complexes are proposed in Fig. 3.



(a) (b)

Fig. 3. Proposed structure of the complexes. (a) (X = Cl for **1a, 2a, 3a, 5a, 6a**; X = OH for **4a**); (b) For complexes **1b, 2b, 3b, 4b, 5b, 6b**

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